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(54) Polymer base blend compositions containing destructurized starch.

(57) A composition of matter capable of being formed into articles having substantial dimensional stability comprising

- a) destructurized starch, and
 - b) at least one polymer selected from the group of copolymers containing vinyl alcohol units together with aliphatic chain units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate, with unsaturated monomers containing no functional group with subsequent hydrolysis of the vinyl ester group.
- The composition may contain further conventional additives as well as hydrophobic, substantially water-insoluble polymers.

POLYMER BASE BLEND COMPOSITIONS CONTAINING DESTRUCTURIZED STARCH

The present invention relates to polymer compositions capable of being formed by heat and pressure into articles having dimensional stability and enhanced physical properties, and to pre-mixes useful for preparing these compositions. These compositions and pre-mixes comprise destructurized starch and other polymers as described herein.

5 It is known that natural starch which is found in vegetable products and which contains a defined amount of water can be treated at an elevated temperature and in a closed volume, thereby at elevated pressures, to form a melt. The process is conveniently carried out in an injection molding machine or extruder. The starch is fed through the hopper onto a rotating, reciprocating screw. The feed material moves along the screw towards the tip. During this process, its temperature is increased by means of
10 external heaters around the outside of the barrel and by the shearing action of the screw. Starting in the feed zone and continuing in the compression zone, the particulate feed becomes gradually molten. It is then conveyed through the metering zone, where homogenization of the melt occurs, to the end of the screw. The molten material at the tip can then be treated further by injection molding or extrusion or any other known technique to treat thermoplastic melts, to obtain shaped articles.

15 This treatment, which is described in the European Patent Application No. 84 300 940.8 (Publication No. 118 240) which patent is incorporated herein by reference, yields a substantially destructurized starch. As described in the above mentioned patent, the reason for this is that the starch is heated above the glass transition and the melting temperatures of its components. As a consequence, a melting and disordering of the molecular structure of the starch granules takes place, so that a substantially destructurized starch is obtained. The expression "destructurized starch" defines starch obtained by such thermoplastic melt formation. Reference is also made to European Patent Applications No. 88810455.1 (Publication No. 298,920), No. 88810548.3 (Publication No. 304,401) and No. 89810046.6 (Publication No. 326,517) which further describe destructurized starch, methods for making it, and uses of it. These application are also incorporated herein by reference.

25 It is preferred that the deconstructurized starch used in the present invention has been heated to a high enough temperature and for a time long enough so that the specific endothermic transition analysis as represented by a differential scanning calorimetry (DSC) curve indicates that a specific relatively narrow peak just prior to oxidative and thermal degradation has disappeared, as described in the above-mentioned European Patent Application No. 89810046.6 (Publication No. 326 517).

30 Destructurized starch is a new and useful material for many applications. An important property is its biodegradability. In humid air, however, deconstructurized starch takes up water from the air, thereby increasing its moisture content. As a consequence, a shaped article made from deconstructurized starch may under such conditions lose its dimensional stability. On the other hand such an article may dry out in low humidity and become brittle.

35 Thermoplastic starch has a unique set of properties and while these are very useful, they may limit its utility in cases where a softer, more resilient or harder, tougher polymer is desired.

Thermoplastic starch as mentioned can be extruded and molded into numerous useful shapes and profiles. However, the processing parameters such as water content, temperature, and pressure are critical and must be narrowly controlled to achieve reproducible quality products. This is a further disadvantage for
40 many applications.

To overcome these potential limitations, it would be useful to increase the dimensional stability over a wide humidity range; to increase the toughness (measured as break energy); to increase the elasticity (measured as elongation); to decrease polymer stiffness (measured as Young's modulus) and increase the hardness.

45 Broadening processing latitude increases the variety of shapes and composites and decreases the need for close controls. It would therefore also be useful to improve the control of the melt strength, e.g. increasing the processing latitude for extruding, injection molding, film blowing or fiber drawing and to control the surface tack and adhesion to other substrates.

Conventional thermoplastic materials are hydrophobic, substantially water-insoluble polymers which are conventionally processed in the absence of water and volatile materials. Starch to the contrary forms a melt in the presence of water but decomposes at elevated temperature, i.e. around 240 °C. It was therefore expected that such a starch melt could not be used as a thermoplastic component together with hydrophobic, substantially water-insoluble polymeric materials not only because starch forms a melt in the presence of water as described above, but also because of its chemical structure and hydrophilic nature.

It has now been found that starch, when heated in a closed volume at proper moisture and temperature

conditions as described above to form a melt of destructureized starch, is substantially compatible in its processing with melts formed by hydrophobic substantially water insoluble thermoplastic polymers and that the two types of molten materials show an interesting combination of properties, especially after the melt has solidified.

5 One very important aspect is the surprisingly improved dimensional stability of such destructureized starch blended with such hydrophobic thermoplastic materials. Such polymer compositions are described in copending European Patent Application No. 89810078.9 (Publication No. 327,505), which is incorporated herein by reference. Although articles made from such compositions possess better dimensional stability than those made from destructureized starch alone, the physical properties of the therein-described 10 compositions are not as good as might be desired for some end uses. In particular, it is important that articles made from destructureized starch compositions retain sufficient strength and dimensional stability to perform their desired function while still being biodegradable after disposal.

It has now been found that articles made from such destructureized starch blended with specific hydrophobic thermoplastic materials as described herein show a surprising increase in all or a part of their 15 physical properties and behaviour of their melts as to overcome the limitations as explained above. Moreover it was surprisingly found that many of the blends described herein show a significantly improved dimensional stability in humid air compared with non-blended destructureized starch whilst retaining a surprisingly high degree of disintegration in contact with liquid water which in consequence leads to a high degree of biodegradability.

20 In order to achieve such properties, it has been found useful to make polymer compositions comprising:
 a) destructureized starch, b) at least one polymer selected from the group of copolymers containing vinyl alcohol units together with aliphatic chain units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate, with unsaturated monomers containing no functional group with subsequent hydrolysis of the vinyl ester group, (referred to herein as "component b"), and optionally c) a substantially 25 water-insoluble polymer different from those defined as component b). In one aspect, the present invention relates to a composition comprising destructureized starch and component b). This composition is useful itself for making finished articles, but it is primarily useful as a "pre-mix" for combining with the substantially water-insoluble polymer. In a second aspect, the invention comprises the ternary composition of destructureized starch, component b), and at least one substantially water-insoluble polymer (component 30 c)). These compositions may be in the form of powdery mixtures of the components, melts, or solid forms. The invention also includes methods for making and using both above described compositions and shaped articles made therefrom.

The compositions of the first aspect of the invention comprise:

35 a) destructureized starch, and
 b) at least one polymer selected from the group of copolymers containing vinyl alcohol units together with aliphatic chain units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate, with unsaturated monomers containing no functional group with subsequent hydrolysis of the vinyl ester group.

Such polymer composition may optionally contain further additives.
 40 Specifically, the first aspect of the present invention is a polymer composition capable of being formed into articles having substantial dimensional stability comprising:

a) destructureized starch, and
 b) at least one polymer selected from the group of copolymers containing vinyl alcohol units together with aliphatic chain units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate, 45 with an unsaturated monomer containing no functional group with subsequent hydrolysis of the vinyl ester groups; said polymer being present in an amount effective to enhance the physical properties of said articles (which amount is sometimes referred to herein as an "effective amount" of component b).

Preferably this polymer composition additionally comprises at least one component c):
 c) a substantially water-insoluble thermoplastic polymer which does not fall within the definition of those 50 compounds defined herein as component b).

The present invention includes said polymer compositions in the form of powdery mixtures of their components, in the form of melts, or in solidified form.

Component b) is chosen as described herein to be substantially compatible with the starch and also to promote the compatibility of component c) with the combination of starch and component b).
 55 The present invention further refers to a method of producing said polymer compositions in the molten or solid form as well as a method of producing shaped articles from said polymer compositions, and to the resulting shaped articles made therefrom.

The polymer compositions of the present invention are prepared by admixing destructureized starch,

component b) and optionally component c) and any further additives. This mixture is then heated in a closed volume to elevated temperatures until a homogeneous melt is obtained, and shaped articles can be formed therefrom.

An alternate method of producing the polymer compositions of the present invention comprises: Heating starch which is in a condition to be destructureized in a closed volume to elevated temperatures and at elevated pressures for a time sufficient to destructureize the starch and form a melt; adding component b) as well as other polymer or polymers and/or additives before, during or after such starch destructureization; and continuing to heat the mixture until a homogenous melt is obtained. It is preferred that component b) and, if desired, component c), as well as other additives be combined with the starch and the combination formed into a melt. The starch in this combination may be already wholly or partially destructureized or the destructureization may take place during melt formation.

The present invention further refers to the process of working said polymer composition under controlled water content, temperature and pressure conditions as a thermoplastic melt wherein said working process is any known process, such as, for example injection molding, blow molding, extrusion, coextrusion, compression molding, vacuum forming, thermoforming or foaming. All of these processes are collectively referred to herein as "forming".

The term "functional group" as used herein includes all known polar groups that may be bound to the polymer chain such as, for example, alkoxy, carboxy, carboxyalkyl, alkyl carboxy, halo, pyrrolidone, acetal, and the like.

The term "unsaturated monomers containing no functional group" includes for example alkenes such as ethylene, isobutylene, propylene. It also includes styrene, as the benzenenucleus is not considered to be a functional group within the scope of this invention.

The term "starch" as used herein includes chemically substantially non-modified starches as for example carbohydrates of natural, vegetable origin, composed mainly of amylose and/or amylopectin. They can be extracted from various plants, examples being potatoes, rice, tapioca, corn (maize), pea, and cereals such as rye, oats and wheat. Preferred is starch made from potatoes, corn, wheat or rice. Mixtures of starches obtained from these sources are contemplated. It further includes physically modified starches such as gelatinized or cooked starches, starches with a modified acid value (pH), e.g. where acid has been added to lower their acid value to a range of about 3 to about 6. Further included are starches, e.g. potato starch, in which the divalent ions like Ca^{+2} or Mg^{+2} -ions associated with the phosphate groups have been partially or completely washed out from the starch or optionally wherein the ions present in the starch have been replaced partially or wholly by the same or different mono- or polyvalent ions. It further includes pre-extruded starches, as described in the above-referenced European Patent Application No. 89810046.6 (Publication No. 326,517).

As described above, it has been found that starches, e.g. with a water content within the range of about 5 to about 40 % by weight based on the weight of the composition, undergo a specific narrow endothermic transition on heating to elevated temperatures and in a closed volume just prior to the endotherm change characteristic of oxidative and thermal degradation. The specific endothermic transition can be determined by differential scanning calorimetric analysis (DSC) and is indicated on the DSC-diagram by a specific relatively narrow peak just prior to the endotherm characteristic of oxidative and thermal degradation. The peak disappears as soon as the mentioned specific endothermic transition has been undergone. The term "starch" includes also treated starches wherein said specific endothermic transition has been undergone. Such starch is described in the European Patent Application 89810046.6 (Publication No. 326,517).

Although at the current time, destructureization of starch requires the presence of water in ranges disclosed herein, the present compositions also contemplate the use of destructureized starch prepared by other methods, e.g. without the use of water.

The water content of such a starch/water composition is preferably about 5 to about 40 % water by weight of the starch/water component and preferably about 5 to about 30 %. However, in order to work with the material near its equilibrium water content to which it gets when it is finally exposed to the free atmosphere, a water content of about 10 to about 22 %, preferably of about 14 to about 18 % by weight calculated based on the starch/water component should be used in processing and is preferred.

The copolymer of the component b) is preferably a synthetic copolymer containing vinyl alcohol units as well as aliphatic units as are obtained by copolymerization of vinyl esters preferably vinyl acetate with monomers preferably ethylene, propylene, isobutylene, and/or styrene with subsequent hydrolysis of the vinyl ester group. Such copolymers and their derivatives are known.

Copolymers thus obtained may have a general formula wherein the number of repeating units varies for each individual type of copolymer and is known per se as e.g. described in "Encyclopaedia of Polymer Science and Technology, Interscience Publ. Vol. 14, 1971".

Preferred copolymers of component b) are those containing vinyl alcohol units and aliphatic chain units as obtained by copolymerization with ethylene and/or propylene, preferably with ethylene.

Such polymers are e.g. ethylene/vinyl alcohol copolymers (EVAL), propylene/vinyl alcohol copolymers.

- Preferred are the ethylene/vinyl alcohol copolymers. The molar ratio of vinyl alcohol units to alkylene is 5 preferably from about 10 : 90 to about 90 : 10. Preferred is a ratio of about 50 : 50 to about 85 : 15 and most preferred about 60 : 40 to about 81 : 19.

A further embodiment of the present invention are those compounds of component b) as named hereinbefore which further contain about 5 to 20 % of polystyrene units calculated to the total weight of the polymer.

- 10 As mentioned above, the polymer composition comprising the components a) and b) optionally contains one or more substantially water insoluble hydrophobic polymers (component c), as well as further additives.

The component c) is a substantially water-insoluble polymer or a mixture of such substantially water-insoluble polymers. Component c) is preferably present in an amount effective to enhance the physical properties of articles made from the composition of the invention (which amount is sometimes referred to 15 herein as an "effective amount" of component c)), for example increase of dimensional stability of final products made therefrom or adjust the degree of biodegradability.

As used herein a "substantially water-insoluble thermoplastic polymer" is a polymer which preferably absorbs less than 10 % of water, preferably less than 5 % per 100 grams of the polymer at room temperature and preferably at a rate of less than 2 % per 100 grams of the polymer at room temperature.

- 20 Examples of substantially water-insoluble thermoplastic materials are polyolefines, such as polyethylene (PE), polyisobutylenes, polypropylenes; vinyl polymers such as poly(vinyl acetates); polystyrenes; polyacrylonitriles (PAN); substantially water-insoluble polyacrylates or polymethacrylates; polyacetals; thermoplastic polycondensates such as polyamides (PA), polyesters, polyurethanes, polycarbonates, poly-(alkylene terephthalates); polyarylethers and thermoplastic polyimides; and high molar-mass, substantially 25 water-insoluble or crystallizable poly(alkylene oxides) such as polymers or copolymers of ethylene oxide and propylene oxide.

Further included are substantially water-insoluble thermoplastic copolymers known such as 30 alkylene/vinyl ester-copolymers preferably ethylene/vinyl acetate-copolymers (EVA); alkylene/acrylates or methacrylate copolymers preferably ethylene/acrylic acid copolymers (EAA); ethylene/ethyl acrylate-copolymers (EEA); ethylene/methyl acrylate-copolymers (EMA); ABS-copolymers; styrene/acrylonitrile-copolymers (SAN); ethylene/maleic anhydride copolymers, acrylic acid esters/acrylonitrile copolymers; acrylamide/acrylonitrile copolymers; block copolymers of amide-ethers, amide-esters; block copolymers of urethane-ethers, urethane-esters; as well as mixtures thereof.

- 35 Preferred from these are those which undergo melt formation at a set processing temperature preferably within the range of about 95 °C to about 260 °C, preferably within the range of about 95 °C to about 220 °C and more preferably within the range of about 95 °C to about 190 °C.

Also preferred are those polymers containing polar groups such as ether, amide, or urethane groups. Such polymers include e.g. copolymers of ethylene, propylene or isobutylene with vinyl compounds containing functional groups such as styrene/acrylo-nitrile-copolymers (SAN); block copolymers of amide-ethers, amide-esters; block copolymers of urethane-ethers, urethane-esters; as well as their mixtures.

- 40 Such substantially water-insoluble thermoplastic polymers may be added in any desired amount as described herein.

Such polymers may be used in any known form. Their molecular weight is also generally known in the art. It is also possible to use such polymers of relatively low molecular weight (oligomers). The choice of a 45 particular molecular weight range is a matter of optimization and routine experimentation known to the one skilled in the art.

- In the composition according to this invention, the two components a) and b) or the three components a), b) and c) always add up to 100 % and the values of the components given in percent hereinbelow refer to the sum of 100 %.

50 The ratio of destructureized starch to component b) and optionally to the sum of components b) and c) can be 1:99 to 99:1. It is however preferred that the destructureized starch contributes noticeably to the properties of the final material. Therefore, it is preferred that the destructureized starch is present in an amount of at least about 10 %, more preferably about 50 % and most preferably in the range of about 60 % to about 90 % by weight of the entire composition. That is, component b) is and optionally the sum of 55 the components b) and c) are present in amounts of about 90 % or less, more preferably less than or equal to about 50 % and most preferably in the range of about 40 % to about 10 % by weight of the entire composition.

Component b) is a relatively polar material. When it functions in the present compositions in combina-

tion with component c), it is able to mix more readily with a more polar component c) than with a less polar one. Accordingly, with more polar components c), relatively less of component b) will be required than with less polar ones. The skilled worker will be able to select appropriate ratios of components b) and c) to obtain a substantially homogenous melt composition.

- 5 If the destructureized starch contains water, the percentage of this destructureized starch component is meant to be the destructureized starch/water component, i.e. including the weight of water.

The starch may be mixed prior to destructureization with additives as named hereinbelow to yield a free flowing powder useful for continuous processing and is destructureized and granulated before it is mixed with component b) or b) and c) or the other optionally added components. The other components to be added 10 are preferably granulated to a granular size equal to that of the granulated destructureized starch.

However, it is possible to process native starch or pre-extruded and/or destructureized granulated or powdered starch together with powdered or granulated additives and/or the polymeric material in any desired mixture or sequence.

Thus, it is preferred that components a), b) and c) as well as other conventional additives be mixed in a 15 standard mixer. This mixture can then be passed through an extruder to produce granulates or pellets as one form of shaped articles which are also useful as starting material for processing into other articles. However, it is possible to avoid granulating and to process the obtained melt directly using down-stream equipment to produce films, blown films included, sheets, profiles, pipes, tubes, foams or other shaped articles. The sheets can be used for thermoforming.

20 It is preferred that fillers, lubricants and/or plasticizers be added to the starch before destructureization. However the addition of coloring agents as well as of the components b), c) and additives other than the aforementioned can be added before, during or after destructureization.

The substantially destructureized starch/water component or granules have a preferred water content in 25 the range of about 10 to about 22 % by weight of the starch/water component, preferably about 12 to about 19 % and most preferably about 14 to about 18 % by weight of the starch/water component.

The water content described above refers to the percentage of water relative to the weight of the starch/water component within the total composition and not to the weight of the total composition itself, which would include also the weight of any added substantially water-insoluble thermoplastic polymer.

In order to destructureize the starch and/or to form a melt of the new polymeric composition according to 30 this invention, it is suitably heated in a screw and barrel of an extruder for a time long enough to effectuate destructureization and melt formation. The temperature is preferably within the range of 105 °C to 240 °C, more preferably within the range of 130 °C to 190 °C depending on the type of starch used. For this destructureization and melt formation, the composition is heated in a closed volume. A closed volume can be a closed vessel or the volume created by the sealing action of the unmolten feed material as happens in the 35 screw and barrel of injection molding or extrusion equipment. In this sense the screw and barrel of an injection molding machine or an extruder is to be understood as being a closed vessel. Pressures created in a closed vessel correspond to the vapour pressure of water at the used temperature but of course additional pressure may be applied and/or generated as normally occurs in a screw and barrel. The preferred applied and/or generated pressures are in the range of pressures which occur in extrusion and are 40 known per se, e.g. from 5 to 150 x 10⁵ N/m² preferably from 5 to 75 x 10⁵ N/m² and most particularly from 5 to 50 x 10⁵ N/m². If the thus-obtained composition is comprised only of destructureized starch, it may be granulated and ready to be mixed with the further components according to a chosen mixing and processing procedure to obtain the granular mixture of the destructureized starch/polymer starting material to be fed to the screw barrel.

45 However, the obtained melt in the screw and barrel may be injection molded directly into a suitable mold, i.e. directly further processed to a final product if all necessary components are already present.

Within the screw, the granular mixture obtained as described above is heated to a temperature which is generally within the range of about 80 °C to about 240 °C, preferably within the range of about 120 °C to about 220 °C and more preferably within the range of about 130 °C to about 190 °C. Preferably, such 50 mixture is heated to a sufficiently high temperature and for a time long enough until the endothermic transition analysis (DSC) indicates that the specific relatively narrow peak just prior to the endotherm characteristic of oxidative and thermal degradation of starch has disappeared.

The minimum pressures under which the melts are formed correspond to the water vapour pressures produced at said temperatures. The process is carried out in a closed volume as explained above, i.e. in 55 the range of the pressures which occur in extrusion or molding processes and known per se, e.g. from zero to 150 x 10⁵ N/m² preferably from zero to 75 x 10⁵ N/m² and most particularly from zero to 50 x 10⁵ N/m².

When forming a shaped article by extrusion the pressures are preferably as mentioned above. If the melt according to this invention is, e.g., injection molded, the normal range of injection pressures used in

injection molding is applied, e.g. from 300×10^5 N/m² to 3000×10^5 N/m² and preferably from 700×10^5 to 2200×10^5 N/m².

Accordingly, the present invention provides a thermoplastic destructurized-starch substantially homogenous melt formed by the process comprising:

- 5 1) providing a mixture comprising starch and at least one polymer selected from the group of copolymers containing vinyl alcohol units together with aliphatic chain units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate, with unsaturated monomers containing no functional group with subsequent hydrolysis of the vinyl ester group;
- 10 2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to effectuate destructureization of said starch and form said melt.

The present invention also provides a thermoplastic destructurized-starch product having substantial dimensional stability formed by the process comprising:

- 15 1) providing a mixture comprising starch and at least one polymer selected from the group of copolymers containing vinyl alcohol units together with aliphatic chain units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate, with unsaturated monomers containing no functional group with subsequent hydrolysis of the vinyl ester group; said polymer being present in an amount effective to enhance the physical properties of said articles (which amount is sometimes referred to herein as an "effective amount" of component b));
- 20 2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to effectuate destructureization of said starch and form a substantially homogenous melt;
- 25 3) shaping said melt into an article; and
- 30 4) allowing said shaped article to cool to a substantially dimensionally stable thermoplastic product.

The mixture provided in step 1) of either above-described processes may additionally contain component c) and additives as described herein.

- 35 25 Various hydrophilic polymers may be used as additives. These include water-soluble and water-swellable polymers. As such it includes animal gelatin, vegetable gelatins proteins such as sunflower protein, soybean proteins, cotton seed proteins, peanut proteins, rape seed proteins, acrylated proteins; water-soluble polysaccharides, alkyl celluloses, hydroxyalkyl celluloses and hydroxyalkylalkyl celluloses, such as methyl cellulose, hydroxymethyl cellulose, hydroxyethyl cellulose, hydroxypropyl cellulose, hydroxylethylmethyl cellulose, hydroxpropylmethyl cellulose, hydroxybutylmethyl cellulose, cellulose esters and hydroxyalkyl cellulose esters such as cellulose acetylphthalate (CAP), hydroxypropylmethyl cellulose (HPMCP); analogous known polymers made from starch; water-soluble or water-swellable synthetic polymers such as: polyacrylates, polymethacrylates, polyvinyl alcohols, shellac and other similar polymers.

Preferred are synthetic polymers, most preferably polyacrylates, polymethacrylates, polyvinyl alcohols.

- 35 35 Such hydrophilic polymers may optionally be added up to about 50 % based on the starch/water component, preferably up to about 30 % and most preferably between about 5 % and about 20 % based on the starch/water component. If any hydrophilic polymer is added, its mass should be considered along with the starch in determining the appropriate amount of water in the composition.

- 40 40 Other useful additives may be e.g. adjuvants, fillers, lubricants, mold release agents, plasticizers, foaming agents, stabilizers, coloring agents, pigments, extenders, chemical modifiers, flow accelerators, and mixtures thereof.

Examples for fillers are inorganic fillers, such as the oxides of magnesium, aluminum, silicon, titanium, etc. preferably in a concentration in the range of about 0.02 to about 50 % by weight preferably about 0.20 to about 20 % based on the total weight of all the components.

- 45 45 Examples for lubricants are stearates of aluminum, calcium, magnesium and tin as well as talc, silicones, etc. which may be present in concentrations of about 0.1 to about 5 % preferably at about 0.1 to about 3 % based upon the weight of the total composition.

- 50 50 Examples of plasticizers include low molecular poly(alkylene oxides), such as poly(ethylene glycols), poly(propylene glycols), poly(ethylene-propylene glycols); organic plasticizers of low molar masses, such as glycerol, pentaerythritol, glycerol monoacetate, diacetate or triacetate; propylene glycol, sorbitol, sodium diethylsulfosuccinate, etc., added in concentrations ranging from about 0.5 to about 15 %, preferably ranging from about 0.5 to about 5 % based on the total weight of all the components. Examples of colouring agents include known azo dyes, organic or inorganic pigments, or colouring agents of natural origin. Inorganic pigments are preferred, such as the oxides of iron or titanium, these oxides, known per se, being added in concentrations ranging from about 0.001 to about 10 %, preferably about 0.5 to about 3 %, based on the weight of all the components.

There may further be added compounds to improve the flow properties of the starch material such as animal or vegetable fats, preferably in their hydrogenated form, especially those which are solid at room

temperature. These fats have preferably a melting point of 50 °C or higher. Preferred are triglycerides of C₁₂ -, C₁₄ -, C₁₆ -, and C₁₈ - fatty acids.

These fats can be added alone without adding extenders or plasticizers.

These fats can advantageously be added alone or together with mono- and/or diglycerides or phosphatides, especially lecithin. The mono- and diglycerides are preferably derived from the types of fats described above, i.e. from C₁₂ -, C₁₄ -, C₁₆ -, and C₁₈ - fatty acids.

The total amount of fats, mono-, diglycerides and/or lecithins used are up to about 5 % and preferably within the range of about 0.5 to about 2 % by weight of the total weight of starch and any added hydrophilic polymer.

10 The materials may further contain stabilizers, such as antioxydants, e.g. thiobisphenols, alkylidene-bisphenols secondary aromatic amines; light stabilizers such as UV-absorbers and UV-quenchers; hydroperoxide decomposer; free-radical scavengers; stabilizers against microorganisms.

15 The compositions of the invention form thermoplastic melts on heating and in a closed volume, i.e. under conditions of controlled water-content and pressure. Such melts can be processed just like conventional thermoplastic materials, using, for example, conventional apparatus for injection molding, blow molding, extrusion and coextrusion (rod, pipe and film extrusion), compression molding, foaming, to produce known articles. The articles include bottles, sheets, films, packaging materials, pipes, rods, laminated films, sacks, bags, pharmaceutical capsules, granules, powders or foams.

20 For example, these compositions may be used to prepare low density packaging materials (e.g. foams) by well-known methods. Conventional blowing agents may be utilized if desired or, for certain compositions, the water itself may act as the blowing agent. Open cell and closed cell foams may be produced as desired by varying the composition and processing conditions. These foams produced from the present compositions will demonstrate improved properties (e.g., dimensional stability, moisture resistance, etc.) when compared with foams made of starch without incorporation of the components b) and c) according to this invention.

25 These compositions may be used as carrier materials for active substances, and may be mixed with active ingredients such as pharmaceuticals and/or agriculturally active compounds such as insecticides or pesticides for subsequent release applications of these ingredients. The resulting extruded materials can be granulated or worked to fine powders.

30 The following examples are provided to further explain and exemplify the invention but not to limit the scope thereof, which scope is defined by the appended claims.

Example 1

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(a) 9500 g of potato starch containing 15.1 % water are placed in a high speed mixer and 3226 g of polyethylene-co-vinyl alcohol (component b) containing 73 mole % of vinyl alcohol and 27 mole % of ethylene sold as EVAL-L-101 by Kuraray; 80.75 g of hydrogenated fat (lubricant release agent) sold as Boeson VP by Boehringer Ingelheim, 40.37 g of a melt flow accelerator (lecithin) sold as Metarin P by Lucas Meyer are added under stirring. The water content of the final mixture is 11.2 %.

(b) 10,000g of the mixture prepared under (a) are fed through a hopper into a Leistritz co-rotating twin screw extruder (model LSM 34 GL).

The temperature profile of the main sections of the barrel is respectively 25 °C/ 90 °C/ 180 °C/ 200 °C/ 160 °C/ 120 °C/ 130 °C.

45 Extrusion is carried out with a mixture output of 8.8 kg/hr (screw speed 200 rpm). Water is added at the inlet with a flow rate of 2.5 kg/hr. The water content of the material during extrusion is therefore 29 %. In the last section of the extruder 200 mbar reduced pressure is applied to remove part of the water as water vapour.

The water content of the granulates is 8.5 % as measured after they have equilibrated at room 50 temperature. They are brought to a water content of 17 % by spraying water under stirring in a conventional mixer.

(c) The granulates of the pre-blended mixture as obtained under (b) (H₂O content: 17 %) are fed through a hopper to an injection molding machine Kloeckner-Ferromatic FM 60 for the production of tensile test pieces. The temperature profile of the barrel is: 90 °C/ 165 °C/ 165 °C/ 165 °C.

55 The shot weight is 8 g, the residence time 450 sec., the injection pressure 800 bar, the back pressure 30 bar, the screw speed 180 rpm.

The tensile test pieces thus produced are conditioned in a climatic cabinet at 50 % R.H. for five days as an arbitrary standard condition.

The test pieces are of standard ISO design (ISO No. R527).

(d) The conditioned tensile test pieces are then tested for their stress/strain behaviour on a Zwick tensile test apparatus.

The samples are measured at room temperature using an extension rate of 10 mm per minute. Results 5 are presented in Table 1 and compared with those of the tensile test pieces obtained from the same starch process d in a similar way but in absence of component b).

Table 1

	unblended starch	Example Nos.				
		1	3	4	5	6
break strain %	22	30	17	13	5	4
break energy KJ/m ²	325	520	290	215	73	52

20

Example 2

Example 1 is repeated except that the ratio of the components is varied as given in Table 2. For comparison perspective, Example 1 is shown as Blend No. 1.

Table 2

Blend No.	starch: component b) + c)	component b): component c)
	(weight ratio)	(weight ratio)
2	50 : 50	100 : 0
3	60 : 40	99 : 1
4	70 : 30	50 : 1
5	80 : 20	20 : 1
Ex.1	91.5: 8.5	10 : 1
6	90 : 10	1 : 1
7	94 : 6	1 : 10
8	98 : 2	1 : 50
9	99 : 1	1 : 99

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The resulting injection molded polymers are tougher and more resistant to humid air than the unmodified starch polymer. The toughness as judged by resistance to breaking upon bending increases from blend 9 to blend 2 in concert with the combined increase in ethylene-vinyl alcohol content. While the resistance to softening in humid atmosphere is improved in all cases relative to unmodified starch, the resistance of blends 1,4,5 and 6 are particularly good. These results illustrate the unexpected combinations 50 as benefits in performance.

Example 3

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Example 1 is repeated by replacing component (b) (EVAL-L-101) with polyethylene-co-vinyl alcohol Clarene L-4 of Solvay containing 71 mole % of vinyl alcohol and 29 mole % of ethylene. The break strain and break energy of the resulting injection molded blend are shown in Table 1. It can be seen that a lower vinyl alcohol content as compared to EVAL-L-101, leads to a decrease in the tensile properties, even lower

than those of starch without component b)).

Example 4

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Example 1 is repeated by replacing component b) (EVAL-L-101) with polyethylene-co-vinyl alcohol EVAL-F-101 of Kuraray containing 68 mole % of vinyl alcohol and 32 mole % of ethylene. The break strain and break energy of the resulting injection molded blend are shown in Table 1. It can be seen that a lower vinyl alcohol content as compared to EVAL-L-101, leads to a decrease in the tensile properties, even lower than those of starch without component b).

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Example 5

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Example 1 is repeated by replacing component b) (EVAL-L-101) with polyethylene-co-vinyl alcohol EVAL-K-102 of Kuraray containing 62 mole % of vinyl alcohol and 38 mole % of ethylene. The break strain and break energy of the resulting injection molded blend are shown in Table 1. It can be seen that a lower vinyl alcohol content as compared to EVAL-L-101, leads to a decrease in the tensile properties, even lower than those of starch without component b).

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Example 6

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Example 1 is repeated by replacing component b) (EVAL-L-101) with polyethylene-co-vinyl alcohol EVAL-E-105 of Kuraray containing 56 mole % of vinyl alcohol and 44 mole % of ethylene. The break strain and break energy of the resulting injection molded blend are shown in Table 1. It can be seen that a lower vinyl alcohol content as compared to EVAL-L-101, leads to a decrease in the tensile properties, even lower than those of starch without component b).

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Example 7

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(a) 5000 g of potato starch containing 15 % water are placed in a high speed mixer and 4250 g of polyethylene-co-vinyl alcohol (component b) sold as EVAL-L-101 by Kuraray and containing 73 mole % of vinyl alcohol and 27 mole % of ethylene; 42.5 g of hydrogenated fat (lubricant release agent) sold as Boeson VP by Boehringer Ingelheim, 21.25 g of a melt flow accelerator (lecithin) sold as Metarin P by Lucas Meyer are added under stirring. The water content of the final mixture is 8.1 %.

(b) 9000g of the mixture prepared under (a) are fed through a hopper into a Werner & Pfleiderer co-rotating twin screw extruder (model Continua 37).

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The temperature profile of the four sections of the barrel is respectively 20 °C/ 80 °C/ 190 °C/ 150 °C.

Extrusion is carried out with a mixture output of 8.8 kg/hr (screw speed 200 rpm). Water is added at the inlet with a flow rate of 2.5 kg/hr. The water content of the material during extrusion is therefore 30 %. In the last section of the extruder 35 mbar reduced pressure is applied to remove part of the water as water vapour.

45

The water content of the granulates is 8.5 % as measured after they have equilibrated at room temperature. They are brought to a water content of 17 % by spraying water under stirring in a conventional mixer.

50

(c) The granulates of the pre-blended mixture as obtained under (b) (H_2O content: 17 %) are fed through a hopper to an injection molding machine Arburg 329-210-750 for the production of tensile test pieces. The temperature profile of the barrel is: 90 °C/ 175 °C/ 175 °C/ 175 °C.

The shot weight is 7.3 g, the residence time 450 sec., the injection pressure 1650 bar, the back pressure 80 bar, the screw speed 180 rpm.

The tensile test pieces thus produced are conditioned in a climatic cabinet at 50 % R.H. for five days as an arbitrary standard condition.

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The test pieces are of standard DIN design (DIN No. 53455).

(d) The conditioned tensile test pieces are then tested for their stress/strain behaviour on a Zwick tensile test apparatus as given in Example 1. Results are presented in Table 3.

Table 3

	unblended starch	Examples Nos.			
		7	8	9	
5	Break Strain (%)	22	150	25	370
10	Break Energy (KJ/m ²)	325	1560	350	1830

Example 8

(a) 9500 g of potato starch containing 15.1 % water are placed in a high speed mixer and 255 g of polyethylene-co-vinyl alcohol (component b) sold as EVAL-F 101 by Kuraray (containing 68 mole % vinyl alcohol and 32 mole % ethylene). 170 g of Nylon 12 (component c)) sold as Vestamid L-1700 by Huels Chemie; 51 g of hydrogenated fat (lubricant/release agent) Boeson VP and 25.5 g of a melt flow accelerator (lecithin/Metarin P) are added under stirring. The water content of the final mixture is 14 %.

(b) 9000 g of the mixture prepared under (a) are fed through a hopper into the same twin-screw co-rotating extruder described in Example 7. The extrusion of the mixture is carried out with the following temperature profile: 20 °C/ 80 °C/ 170 °C/ 80 °C. The other parameters of the extrusion experiment are the following:

material output: 9.1 kg/hr

screw speed: 200 rpm

water added: 1.4 kg/hr

reduced pressure (last section) 30 mbar

water-content during extrusion: 26.8 %

The water content of the granulates is 14.5 % as measured after they have equilibrated at room temperature. They are brought to a water content of 17 % H₂O by spraying water under stirring in a conventional mixer.

(c) The granulates obtained under (b) are processed using the same injection molding machine described in (c) of Example 7. The temperature profile of the barrel is 90 °C/ 155 °C/ 155 °C/ 155 °C. The other processing parameters are:

shot weight: 8 g

residence time: 450 sec.

injection pressure: 2200 bar

back pressure: 80 bar

screw speed: 180 rpm

The tensile test pieces thus produced are conditioned and tested on a Zwick tensile test apparatus as described in (d) of Example 1.

Results are presented in Table 3.

Example 9

(a) 2000 g of potato starch containing 15.2 % water are placed in a high speed mixer and 850 g of polyethylene-co-vinyl alcohol (component b) (EVAL-L-101 of Kuraray) containing 73 mole % vinyl alcohol and 27 mole % ethylene; 5950 g of polyamide-block-polyether (component c) sold as Pebax MA-4011 by Atochem; 17 g of hydrogenated fat (lubricant/ release agent) Boeson VP; 8.5 g of a melt flow accelerator (lecithin) Metarin P are added under stirring. The water content of the final mixture is 3.4 %.

(b) 8000 g of the mixture prepared under (a) are fed through a hopper into the same twin-screw co-rotating extruder described in Example 7.

The extrusion of the mixture is carried out with the following processing parameters:

temperature profile: 20 °C/ 80 °C/ 220 °C/ 180 °C

material output: 8.8 kg/hr

screw speed: 200 rpm

water added: 1.8 kg/hr

reduced pressure (last section): 33 mbar

water content during extrusion: 21.1 %

- 5 The water content of the granulates is 8.5 % after they have equilibrated at room temperature. They are brought back to a water content of 17 % H₂O by spraying water under stirring in a conventional mixer.

(c) The granulates of (b) are processed using the same injection molding machine of Example 7. The processing parameters are the following:

temperature profile: 90 °C/ 165 °C/ 165 °C/ 165 °C

- 10 shot weight: 6.6 g

residence time: 450 sec

injection molding: 1100 bar

back pressure: 80 bar

screw speed: 180 rpm

- 15 The tensile test pieces thus produced are conditioned and tested on a Zwick tensile test apparatus described in (d) of Example 1.

Results are presented in Table 3.

20 Example 10

Example 9 is repeated by replacing component c) with a thermoplastic polyurethane elastomer sold as Pellethane 2103-80-AEF by Dow Chemical Company. The resulting injection molded polymer is tougher than unblended starch polymer.

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Example 11

- Example 7 is repeated but in addition to EVAL-L-101 (component b)) 170 g of polyethylene Lupolen 30 2410 T of BASF are added to the starch. The resulting injection molded polymer has stress-strain properties similar to the material obtained in Example 7 i.e. it is considerably tougher than the unblended starch polymer.

35 Example 12

Example 8 is repeated but component c) is replaced by polyethylene-co-vinyl acetate (80 mole % ethylene, 20 mole % vinyl acetate), Escorene UL 02020 sold by Exxon.

The ratio of the components is varied as given in Table 4.

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Table 4

45	Blend No.	starch: component b) + c)	component b): component c)
		(weight ratio)	(weight ratio)
50	2	50 : 50	1 : 10
	3	60 : 40	1 : 20
	4	70 : 30	1 : 50
	5	80 : 20	1 : 99
	6	90 : 10	10 : 1
	7	94 : 6	20 : 1
	8	98 : 2	50 : 1
55	9	99 : 1	100 : 1

The resulting injection molded polymers are tougher than the unblended starch polymers.

Example 13

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Example 1 (Sections a) and b)) is repeated except that the water content is adjusted to 22 %, and the cutter is removed from the die face. A continuous extrudate is obtained which is foamed as a result of the excess water evaporation. The foam is chopped into 30-40 mm lengths and is useful as a loose-fill, packaging insulation material.

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Example 14

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During each of the injection molding operations in Examples 2 - 12 an experiment is performed to demonstrate the utility of making foams. The molten material is obtained as described in Example 1 or 7, Sections a), b) and c) in each case is extruded into the open atmosphere (Section c) instead of being injection molded into a closed mold. In every case the material is converted into a foamed extrudate useful for loose-fill in packaging applications.

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Example 15

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The granulates from Example 1 or 7 are mixed with polystyrene in the proportion of 30 to 70 parts by weight and are treated according to Example 14. The resulting foamed extrudate contains a very fine and uniform cell structure suitable for a variety of uses including structural foam.

Claims

- 30 1. A composition of matter capable of being formed into articles having substantial dimensional stability comprising
 - a) destructureized starch, and
 - b) at least one polymer selected from the group of copolymers containing vinyl alcohol units together with aliphatic chain units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate, with unsaturated monomers containing no functional group with subsequent hydrolysis of the vinyl ester group.
- 35 2. A composition according to claim 1 wherein said component b) is a copolymer as is obtained by copolymerization of vinyl acetate with ethylene, propylene, isobutylene, and/or styrene with subsequent hydrolysis of the vinyl ester group.
- 40 3. A composition according to claim 2 wherein the component b) is a copolymer as is obtained by copolymerization of vinyl acetate with ethylene and/or propylene with subsequent hydrolysis of the vinyl ester group.
- 45 4. A composition according to claim 3 wherein the component b) is a copolymer as is obtained by copolymerization of vinyl acetate with ethylene with subsequent hydrolysis of the vinyl ester group.
- 50 5. A composition according to anyone of the claims 1 to 4 wherein the molar ratio of vinyl alcohol units to alkylene units is from about 10 : 90 to about 90 : 10, preferably from about 50 : 50 to about 85 : 15, and preferably from about 60 : 40 to about 81 : 19.
- 55 6. A composition according to anyone of the claims 1 to 5 wherein the component b) further contains about 5 to 20 % of polystyrene units calculated to the total weight of the polymer.
7. The composition according to anyone of the claims 1 to 6 wherein the weight % ratio of destructureized starch to component b) is about 1:99 to about 99:1.
8. The composition according to claim 7 wherein destructureized starch is present in amounts of about 50 % to about 99 % of the total composition.
9. The composition according to anyone of the claims 1 to 8 wherein the destructureized starch has a water content of about 5 % to about 40 % by weight of the total starch content, preferably of about 10 % to about 22 % by weight of the total starch content.
- 55 10. The composition according to anyone of the claims 1 to 9 wherein there is additionally incorporated component c) comprising a substantially water-insoluble thermoplastic polymer which does not fall within

the definition of those compounds defined as component b).

11. The composition according to claim 10 wherein said component c) is selected from the group consisting of polyolefines, vinyl polymers, polystyrenes, polyacrylonitriles, polyacrylates, polymethacrylates, polyacetals, thermoplastic polycondensates, polyarylethers, thermoplastic polyimides, substantially water-insoluble or crystallizable poly(alkylene oxides), and mixtures thereof.
- 5 12. The composition of claim 10 wherein component c) is selected from the group consisting of polyethylenes, polypropylenes, polyisobutylenes, poly(vinyl chlorides), poly(vinyl acetates), polystyrenes; polyamides, polyesters, polyurethanes, polycarbonates, poly(alkylene terephthalates).
- 10 13. The composition according to claim 10 wherein component c) is selected from the group consisting of alkylene/vinyl ester-copolymers, alkylene/acrylate or methacrylate copolymers, ABS copolymers, styrene/acrylonitrile copolymers, alkylene/maleic anhydride copolymers, acrylic acid esters/acrylonitrile copolymers, acrylamide/ acrylonitrile copolymers, block copolymers of amide-ethers, amide-esters; block copolymers of urethane-esters and mixtures thereof.
- 15 14. The composition according to claim 10 wherein component c) is selected from the group consisting of ethylene/vinyl acetate copolymers (EVA), ethylene/acrylic acid copolymers (EAA), ethylene/ethyl acrylate copolymers (EEA), ethylene/methacrylate copolymers (EMA), styrene/acrylonitrile copolymers (SAN), ethylene/maleic anhydride copolymers, block copolymers of amide-ethers, amide-esters; block copolymers of urethane-ethers, urethane-esters and mixtures thereof.
- 20 15. The composition according to anyone of the claims 10 to 14 wherein the sum of components b) and c) constitute about 1 % to about 99 % by weight of the total composition, preferably about 20 % to about 80 % by weight of the total composition, and preferably about 1 % to about 30 % by weight of the total composition.
- 25 16. The composition according to anyone of the claims 1 to 15 wherein there are additionally incorporated one or more materials selected from the group consisting of adjuvants, fillers, lubricants, mold release agents, plasticizers, foaming agents, stabilizers, extenders, chemical modifiers, flow accelerators, coloring agents, pigments and mixtures thereof.
17. The composition according to anyone of the claims 1 to 16 further containing an agriculturally active compound.
- 30 18. The composition according to anyone of the claims 1 to 17 which is a melt blend.
19. The composition according to anyone of the claims 1 to 17 which is a cooled solidified blend.
- 35 20. The composition according to claim 19 in particulate, granulated or pelletized form.
21. A thermoplastic destructureized-starch product made from a composition according to anyone of the claims 1 to 17 and 20 having substantial dimensional stability formed by the process comprising:
- 35 1) providing a mixture comprising at least one polymer selected from the group of copolymers containing vinyl alcohol units together with aliphatic chain units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate, with unsaturated monomers containing no functional group with subsequent hydrolysis of the vinyl ester group;
- 2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to effectuate destructureization of said starch and form a substantially homogenous melt;
- 40 3) shaping said melt into an article; and
- 4) allowing said shaped article to cool to a substantially dimensionally stable thermoplastic product.
22. The product according to claim 21 wherein destructureization of the starch is carried out at a temperature above its melting point and glass transition temperature.
23. The product according to claim 20 or 21 wherein the destructureization of the starch is carried out at temperatures of about 105 °C to about 240 °C, preferably at temperatures of about 130 °C to about 190 °C.
- 45 24. The product according to claim 23 wherein the melt is formed under the range of pressure from the minimum pressure necessary to avoid formation of water vapour under the applied temperature up to about 150 x 10⁵ N/m².
25. The product according to claim 24 wherein the heat and pressure are maintained until the starch has undergone the specific narrow endothermic transition just prior to its endothermic change characteristic of oxidative and thermal degradation.
26. The product according to anyone of the claims 21 to 25 which is a granulate, a pellet or a powder.
27. The product according to claim 26 further melted and processed to form a shaped article selected from the group consisting of containers, bottles, pipes, rods, packaging material, sheets, foams, films, sacks, bags and pharmaceutical capsules.
- 55 28. The shaped articles according to claim 27 wherein the further melting and processing comprises foaming, filming, compression molding, injection molding, blow molding, extruding, co-extruding, vacuum forming, thermoforming and combinations thereof.

29. A thermoplastic destructureized-starch substantially homogenous melt made from a composition according to anyone of the claims 1 to 17, 19 or 20 formed by the process comprising:

1) providing a mixture comprising starch and at least one polymer selected from the group of copolymers containing vinyl alcohol units together with aliphatic chain units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate, with unsaturated monomers containing no functional group with subsequent hydrolysis of the vinyl ester group;

5 2) heating said mixture in a closed volume under sufficient temperature and pressure for a time long enough to destructure said starch and form said melt.

30. The melt according to claim 29 wherein destructureization of the starch is carried out at a temperature of about 105 °C to about 240 °C, preferably at a temperature of about 130 °C to about 190 °C.

10 31. The melt according to claim 29 wherein the melt is formed under the range of pressure from the minimum pressure necessary to avoid formation of water vapour under the applied temperature up to about 150 x 10⁵ N/m²

15 32. The melt according to claim 31 wherein the heat and pressure are maintained until the starch has undergone the specific narrow endothermic transition just prior to its endothermic change characteristic of oxidative and thermal degradation.

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(56) Polymer base blend compositions containing destructureized starch.

(57) A composition of matter capable of being formed into articles having substantial dimensional stability comprising

a) destructureized starch, and

b) at least one polymer selected from the group of copolymers containing vinyl alcohol units together with aliphatic chain units as are obtained by copolymerization of vinyl esters, preferably vinyl acetate, with unsaturated monomers containing no functional group with subsequent hydrolysis of the vinyl ester group.

The composition may contain further conventional additives as well as hydrophobic, substantially water-insoluble polymers.

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EUROPEAN SEARCH
REPORT

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DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
E	EP-A-0 400 532 (BUTTERFLY) "The whole document" -----	1-32	C 08 L 3/02 // (C 08 L 3/02 C 08 L 29:04 C 08 L 23:08) (C 08 L 3/02 C 08 L 29:04 C 08 L 25:06)
A	US-A-3 652 542 (E.T. HJERMSTAD) -----		
D,P,X	EP-A-0 327 505 (WARNER-LAMBERT CO.) "The whole document" -----	1-32	
A	FR-A-2 617 857 (ROTTERDAM MANAGEMENT SERVICES) -----		

The present search report has been drawn up for all claims

Place of search	Date of completion of search	Examiner
The Hague	18 March 91	LESEN H.W.M.
CATEGORY OF CITED DOCUMENTS		
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